

## Ambipolar Diffusion in Semiconductors

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ABSTRACT

Ter Haar has shown that simple kinetic theory arguments based on Drude's early work can be used to derive approximate expressions for the transport properties of semiconductors and metals. Using ter Haar's ideas, this paper derives an expression for the ambipolar diffusion contribution to the electron thermal conductivity. In the first part of the derivation a general expression is obtained for the heat conductivity, using the concepts of the kinetic theory of gases and assuming an electron mean free path. The expression obtained is in all respects similar to the diffusion equation from the kinetic theory of gases, except for a term taking the effect of an electric field into consideration. In the second part of the derivation the concepts of band theory and semiconductor statistics are introduced in the kinetic theory equations. The final expression for the ambipolar contribution, using Boltzmann statistics agrees, except for numerical constants, with the exact form derived from considerations based upon the Boltzmann transport equation. The application of Fermi-Dirac statistics to the problem yields no ambipolar diffusion term as a correction to the conductivity, if terms higher than the first order of the reciprocal of the reduced Fermi level are neglected. This is in agreement with the exact results based upon the Boltzmann transport equation from which it is seen that the ambipolar term contains only second and higher order terms of the reciprocal of the reduced Fermi-level.

### I. INTRODUCTION

THE rapid development of semiconducting materials in recent years and their application to energy conversion devices has stimulated much interest in the transport processes in solids. Solid-state energy conversion devices are, like all heat engines, limited in their efficiency by the Carnot efficiency, and in addition by the transport properties of the solid. The heat conductivity plays a vital part in this process since it limits the amount of heat available for conversion to electrical energy by determining the amount of heat originally absorbed from a heat source and the amount ultimately rejected to a heat sink, and thereby lost. Analysis of the heat conduction process by formal transport theory (assumption of relaxation time), in the region of mixed conduction, shows that the heat conductivity is not simply the sum of the electron and hole conductivities. An additional term appears, which is proportional to the carrier mobilities and a quadratic term involving the ratio of the band-gap energy  $\Delta E$  to the average kinetic energy, and inversely proportional to the sum of the hole and electron mobility. This term represents a contribution to the heat conductivity which is especially marked when the band-gap  $\Delta E$  is much larger than the average energy of the carriers.

The mathematical apparatus required to arrive at the expression for the heat conductivity and the ambipolar diffusion term is considerable and it is instructive to see just how far one can go using a very simple model for the transport processes in a solid. Ter Haar<sup>1</sup> has shown that using simple kinetic theory arguments, first-order approximations can be obtained for the electrical conductivity, heat conductivity, thermoelectric power, etc., of metals and semiconductors. In fact the basic equations are identical to the equations of thermal conductivity, viscosity, and diffusion derived from the kinetic theory of gases. Although the model is very crude indeed, it yields first-order terms even for the complicated transport phenomena which occur in the presence of temperature and density gradients. Ter Haar makes a number of simplifying assumptions in his calculations which upon more careful examination can be shown to restrict the full power of his approach unnecessarily. For example, ter Haar<sup>1</sup> calculates the absolute thermoelectric power of a semiconductor and gets the dominant term proportional to the average kinetic energy of the carriers—more careful analysis turns up the missing term proportional to the Fermi energy transported

<sup>1</sup> D. ter Haar, *Physica* 22, 61 (1956).

by the carriers.<sup>2</sup> We therefore thought it worthwhile to take another look at the problem of the ambipolar contribution to heat conduction in intrinsic semiconductors. Ter Haar's calculation of the ambipolar effect yields the relatively large term proportional to  $(k/e)^2(|\Delta E|/kT)^2$ . But careful recalculation of the problem gives an expression which contains in addition to the term given by ter Haar, contributions proportional to  $(k/e)^2(|\Delta E|/kT)$  and to the constant  $(k/e)^2$ . (This constant is in effect equal to twice the Lorentz number.<sup>3</sup>) This accounts for all the terms found by the usual solution of the transport equations except for numerical constants. The same analysis is extended to a degenerate gas. The case of ambipolar diffusion in a semimetal is considered, and the results of calculations are given.

The analysis presented by ter Haar and elaborated here is, of course, an extension of the very old but nonetheless still interesting Drude theory of metals.<sup>4</sup> The analysis is neither intended nor pretends to replace results derived from a solution of the Boltzmann transport equation, but attempts to show that a very simple physical model does remarkably well in reproducing some result of solid-state theory.

We proceed with the calculation of the electric and thermal current densities assuming the semiconductor or semimetal to be a gas of electrons and holes of density  $n_1$  and  $n_2$ , respectively. In the calculations all pretense of being able to calculate numerical factors is dropped and we henceforth neglect them.

## II. ELECTRIC AND HEAT CURRENT DENSITY

### 1. General Formulation

Consider particles passing through an imaginary plane at  $x$  in the positive  $x$  direction. The plane is perpendicular to the axis. If  $v_1$  is the average velocity of the particles at the plane, the velocity  $v_1(x-\lambda_1)$  of the particles having suffered a collision at distance  $\lambda_1$  from the plane will be that appropriate to the last collision, i.e.,

<sup>2</sup> F. E. Geiger, NASA TN D-1176, May 1962 (unpublished).

<sup>3</sup> In our approximation, where no attempt is made to calculate numerical constants, twice the Lorentz number comes out to be just  $(k/e)^2$ .

<sup>4</sup> P. Drude, Ann. Physik (4), 1, 566 (1900); and (4), 3, 369 (1900).

$v_1(x-\lambda_1) = v_1 - \lambda_1(\partial v_1/\partial x)$ .<sup>5</sup> If the particles are subject to an electric field  $\mathcal{E}_x$ , the velocity of the particles increases by  $\mu_1 \mathcal{E}_x$  over the mean free path  $\lambda_1$ , and the average velocity of the particles crossing the plane in the positive  $x$  direction is<sup>3</sup>

$$v_{1+} = v_1(x-\lambda_1) + \mu_1 \mathcal{E}_x = v_1 - \lambda_1(\partial v_1/\partial x) + \mu_1 \mathcal{E}_x, \quad (1)$$

where  $\mu_1 = e_1 \lambda_1 / m_1 v_1$  is the mobility of the carrier of charge  $e_1$ . The average concentration corresponding to the last collision before the particle passes through the plane, in analogy to our preceding arguments, is

$$n_{-1} = n_1(x-\lambda_1) = n_1 - \lambda_1(\partial n_1/\partial x). \quad (2)$$

The negative particle current density in the positive  $x$  direction can now be written, with the help of Eqs. 1 and 2:

$$j_{x+} = e_1 n_{-1} v_{1+}. \quad (3)$$

The complete expression for the current density contributed by both positive and negative carriers (i.e., holes and electrons) flowing in both the positive and negative  $x$  directions is

$$j_x = e_1 [n_{1-} v_{1+} - n_{1+} v_{1-}] + e_2 [n_{2-} v_{2+} - n_{2+} v_{2-}], \quad (4)$$

where the subscript 2 refers to the positive carriers or holes. This equation can be reduced with the help of the explicit expressions for  $n_{1-}$ ,  $n_{1+}$ , etc., and we get

$$j_x = e \left[ \mathcal{E}_x (n_1 \mu_1 - n_2 \mu_2) - \left( n_1 \lambda_1 \left( \frac{\partial v_1}{\partial x} \right) - n_2 \lambda_2 \left( \frac{\partial v_2}{\partial x} \right) \right) - \left( \lambda_1 v_1 \left( \frac{\partial n_1}{\partial x} \right) - \lambda_2 v_2 \left( \frac{\partial n_2}{\partial x} \right) \right) \right], \quad (5)$$

with  $e_1 = -e_2 = e$ . This equation is interesting in a number of ways. Except for the mobility terms, it is identical with the expression for the rate of mutual diffusion of two ideal gases.<sup>6</sup> Note that the equation contains both the Einstein-diffusion and the thermal-diffusion coefficients. This becomes clear if we write

$$e \lambda v (\partial n / \partial x) = (e \lambda / m v) m v^2 (\partial n / \partial x). \quad (6)$$

<sup>5</sup> The symbols and conventions are those used by ter Haar.

<sup>6</sup> R. Fuerth, Proc. Roy. Soc. A 179, 461 (1942).

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For a classical gas this becomes  $\mu kT(\partial n/\partial x) = eD(\partial n/\partial x)$ , where  $D$  is the Einstein-diffusion coefficient.<sup>7</sup> Similarly transforming  $en\lambda(\partial v/\partial x)$  we get

$$\begin{aligned} en\lambda\left(\frac{\partial v}{\partial x}\right) &= n\left(\frac{e\lambda}{mv}\right)\left(\frac{\partial(mv^2/2)}{\partial x}\right) \\ &= n\mu\left(\frac{\partial(mv^2/2)}{\partial T}\right)\left(\frac{\partial T}{\partial x}\right) = n\mu k\left(\frac{\partial T}{\partial x}\right) \\ &= enD'\left(\frac{\partial T}{\partial x}\right), \end{aligned} \quad (7)$$

where  $D'$  is the thermal diffusion coefficient.<sup>7</sup> Equation 5 may be transformed with the use of Eqs. 6 and 7:

$$\begin{aligned} j_x &= e\mathcal{E}_x(n_1\mu_1 - n_2\mu_2) - \left[ n_1\mu_1\left(\frac{\partial(m_1v_1^2/2)}{\partial x}\right) \right. \\ &\quad \left. + n_2\mu_2\left(\frac{\partial(m_2v_2^2/2)}{\partial x}\right) \right] \\ &\quad - \left[ \mu_1(m_1v_1^2)\left(\frac{\partial n_1}{\partial x}\right) + \mu_2(m_2v_2^2)\left(\frac{\partial n_2}{\partial x}\right) \right]. \end{aligned} \quad (8)$$

It should be emphasized again that Eq. 8 is an approximate equation for the current. If we designate the kinetic energies of the particles by  $\epsilon_1 = (m_1v_1^2/2)$  and  $\epsilon_2 = (m_2v_2^2/2)$ , Eq. 8 becomes

$$\begin{aligned} j_x &= e\mathcal{E}_x(n_1\mu_1 - n_2\mu_2) - \left[ n_1\mu_1\left(\frac{\partial\epsilon_1}{\partial x}\right) + n_2\mu_2\left(\frac{\partial\epsilon_2}{\partial x}\right) \right] \\ &\quad - 2\left[ \mu_1\epsilon_1\left(\frac{\partial n_1}{\partial x}\right) + \mu_2\epsilon_2\left(\frac{\partial n_2}{\partial x}\right) \right], \end{aligned} \quad (9)$$

or, introducing the temperature gradient  $\partial T/\partial x$ ,

$$\begin{aligned} j_x &= e\mathcal{E}_x(n_1\mu_1 - n_2\mu_2) - \left[ \left[ n_1\mu_1\left(\frac{\partial\epsilon_1}{\partial T}\right) + n_2\mu_2\left(\frac{\partial\epsilon_2}{\partial T}\right) \right] \right. \\ &\quad \left. + 2\left[ \mu_1\epsilon_1\left(\frac{\partial n_1}{\partial T}\right) + \mu_2\epsilon_2\left(\frac{\partial n_2}{\partial T}\right) \right] \right] \left(\frac{\partial T}{\partial x}\right). \end{aligned} \quad (10)$$

<sup>7</sup> O. Madelung, "Halbleiter" in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20, p. 86.

The preceding discussion of the equation for the current density allows us now to write down the formal equation for the total heat-current density,  $W_x$ ,

$$\begin{aligned} W_x &= [n_1E_1v_{1+} - n_{1+}E_{1+}v_{1-}] \\ &\quad + [n_2E_2v_{2+} - n_{2+}E_{2+}v_{2-}], \end{aligned} \quad (11)$$

where  $E_{i\pm} = E_i \pm \lambda_i(\partial E_i/\partial x)$ ,  $E_i$  being the total average energy of the particle, i.e., the sum of the kinetic and "potential" energy, and  $n_{i\pm}$  and  $v_{i\pm}$  are as before. If we now substitute the expressions for  $n_i$ ,  $v_i$ , and  $E_i$  in Eq. 11, we get,

$$\begin{aligned} W_x &= \left[ -E_1\lambda_1v_1\left(\frac{\partial n_1}{\partial x}\right) - \lambda_1n_1v_1\left(\frac{\partial E_1}{\partial x}\right) \right. \\ &\quad \left. - n_1E_1\lambda_1\left(\frac{\partial v_1}{\partial x}\right) \right] \\ &\quad + \left[ n_1E_1\mu_1 - \lambda_1^2\mu_1\left(\frac{\partial n_1}{\partial x}\right)\left(\frac{\partial E_1}{\partial x}\right) \right] \mathcal{E}_x \\ &\quad + \text{identical terms except with subscript} \\ &\quad \text{"2", replacing the subscript "1"}. \end{aligned} \quad (12)$$

Using Eqs. 6 and 7, and neglecting terms such as  $(\partial n/\partial x)(\partial E/\partial x)$  and terms of higher orders in  $\partial T/\partial x$ , we write,

$$\begin{aligned} W_x &= e^{-1} \left[ -2E_1\mu_1\epsilon_1\left(\frac{\partial n_1}{\partial T}\right) - 2n_1\mu_1\epsilon_1\left(\frac{\partial E_1}{\partial T}\right) \right. \\ &\quad \left. - n_1\mu_1E_1\left(\frac{\partial\epsilon_1}{\partial T}\right)\right] \left(\frac{\partial T}{\partial x}\right) + [n_1\mu_1E_1] \mathcal{E}_x \\ &\quad + e^{-1} \left[ -2E_2\mu_2\epsilon_2\left(\frac{\partial n_2}{\partial T}\right) - \dots \right] \left(\frac{\partial T}{\partial x}\right) \\ &\quad + [n_2E_2\mu_2] \mathcal{E}_x. \end{aligned} \quad (13)$$

The charge flow caused by the temperature and density gradients sets up an electric field  $\mathcal{E}_x$ , which reduces the current flow to zero, when equilibrium is reached. The magnitude of this field may be obtained from Eq. 10 by setting the

current density  $j_x$  equal to zero and solving for the field  $\mathcal{E}_x$ ,

$$\mathcal{E}_x = \sigma^{-1} \left[ \left[ n_1 \mu_1 \left( \frac{\partial \epsilon_1}{\partial T} \right) + n_2 \mu_2 \left( \frac{\partial \epsilon_2}{\partial T} \right) \right] + 2 \left[ \mu_1 \epsilon_1 \left( \frac{\partial n_1}{\partial T} \right) + \mu_2 \epsilon_2 \left( \frac{\partial n_2}{\partial T} \right) \right] \right] \left( \frac{\partial T}{\partial x} \right), \quad (14)$$

where  $\sigma$ , the electrical conductivity, is given by,<sup>8</sup>

$$\sigma = \sigma_1 + \sigma_2 = e(n_1 \mu_1 + n_2 \mu_2). \quad (15)$$

The heat conductivity is defined for the equilibrium condition  $j_x = 0$ , and Eq. 14 gives the appropriate electric field  $\mathcal{E}_x$ . Substituting Eq. 14 into Eq. 13, we find for the heat current density  $W_x$ ,

$$\begin{aligned} W_x \sigma \left( \frac{\partial T}{\partial x} \right)^{-1} &= \left[ 2E_1 \mu_1 n_2 \mu_2 \epsilon_1 \left( \frac{\partial n_1}{\partial T} \right) - 2n_1^2 \mu_1^2 \epsilon_1 \left( \frac{\partial E_1}{\partial T} \right) \right. \\ &\quad + 2n_1 \mu_1 n_2 \mu_2 \epsilon_1 \left( \frac{\partial E_1}{\partial T} \right) + n_1 \mu_1 n_2 \mu_2 E_1 \left( \frac{\partial \epsilon_1}{\partial T} \right) \\ &\quad \left. + n_1 \mu_1 n_2 \mu_2 E_1 \left( \frac{\partial \epsilon_2}{\partial T} \right) + 2n_1 \mu_1 \mu_2 E_1 \epsilon_2 \left( \frac{\partial n_2}{\partial T} \right) \right] \\ &\quad + [\text{identical expression for holes, except} \\ &\quad \text{all subscripts interchanged}]. \quad (16) \end{aligned}$$

The final reduction of Eq. 16 is quite tedious, and henceforth only the most important steps in the derivation of the heat conductivity is given. We consider now the cases of classical and Fermi-Dirac statistics.

## 2. The Classical Case

If we first consider the case of an intrinsic semiconductor of bandgap  $|\Delta E|$ , the total energy of the electrons is<sup>9</sup>  $E_1 = \epsilon_1$ , and that of the holes  $E_2 = |\Delta E| + \epsilon_2$ . We make use of the equipartition theorem: that is, the average kinetic energy of the electrons equals that of the

holes, or  $\epsilon_1 = \epsilon_2$ , which for classical statistics<sup>10</sup> equals  $(kT)$ , and we get from Eq. 16,

$$\begin{aligned} W_x \sigma \left( \frac{\partial T}{\partial x} \right)^{-1} &= \left[ 2\mu_1 n_2 \mu_2 k^2 T^2 \left( \frac{\partial n_1}{\partial T} \right) - 2n_1^2 \mu_1^2 k^2 T \right. \\ &\quad \left. + 4n_1 \mu_1 n_2 \mu_2 k^2 T + 2n_1 \mu_1 \mu_2 k^2 T^2 \left( \frac{\partial n_2}{\partial T} \right) \right] \\ &\quad + [\text{identical expression for holes, except} \\ &\quad \text{all subscripts interchanged}] \\ &\quad + 2 \left[ n_1 \mu_1 \mu_2 |\Delta E| k T \left( \frac{\partial n_2}{\partial T} \right) + n_1 \mu_1 n_2 \mu_2 |\Delta E| k \right. \\ &\quad \left. + \mu_1 n_2 \mu_2 |\Delta E| k T \left( \frac{\partial n_1}{\partial T} \right) \right]. \quad (17) \end{aligned}$$

The well-known expression for the carrier concentration in the conduction and valence band of an intrinsic nondegenerate semiconductor,<sup>11</sup>  $n_1 = n_2 = 2(2\pi m k T / h^2)^{3/2} e^{-(|\Delta E|/2kT)}$ ,  $m_1 = m_2 = m$ , allows us readily to calculate the gradients  $(\partial n_1 / \partial T)$ , and  $(\partial n_2 / \partial T)$  (again omitting numerical factors),

$$\left( \frac{\partial n_1}{\partial T} \right) = n_1 \left( \frac{1}{T} + \frac{|\Delta E|}{kT^2} \right),$$

and

$$\left( \frac{\partial n_2}{\partial T} \right) = n_2 \left( \frac{1}{T} + \frac{|\Delta E|}{kT^2} \right).$$

Using Eq. 17, we may now write the expression for the heat current density (this time omitting all numerical factors):

$$\begin{aligned} W_x \sigma \left( \frac{\partial T}{\partial x} \right)^{-1} &= -k^2 T \left\{ [n_1^2 \mu_1^2 + n_2^2 \mu_2^2 - n_1 \mu_1 n_2 \mu_2] - n_1 \mu_1 n_2 \mu_2 \right. \\ &\quad \left. - n_1 \mu_1 n_2 \mu_2 \frac{|\Delta E|}{kT} - n_1 \mu_1 n_2 \mu_2 \frac{(|\Delta E|)^2}{(kT)^2} \right\} \\ &= -k^2 T e^{-2} \left\{ [\sigma_1 + \sigma_2]^2 + \sigma_1 \sigma_2 \left[ 1 + \frac{|\Delta E|}{kT} \right]^2 \right\}, \quad (18) \end{aligned}$$

<sup>8</sup> This notation differs from the accepted one in the definition of mobilities, but is used here to facilitate study and comparison with ter Haar's paper.

<sup>9</sup> In the calculation it makes no difference whether we add the "ionization energy"  $|\Delta E|$  to  $\epsilon_1$  or  $\epsilon_2$ .

<sup>10</sup> The factor  $(\frac{3}{2})$  has been omitted in the expression for the average kinetic energy since no attempt is made to calculate numerical constants.

<sup>11</sup> R. A. Smith, *Semiconductors* (Cambridge University Press, Cambridge, England, 1959), p. 78.

where  $\sigma_1$  and  $\sigma_2$  are the electron and hole conductivities, respectively, as defined above. Equation 18 gives all the essential terms in the expression for the heat current density of an intrinsic nondegenerate semiconductor which are obtained by the solution of the Boltzmann transport equation. See, for example, the exact expression obtained by Madelung,<sup>12</sup> also compare with exact results obtained by Price<sup>13</sup> by considering diffusion down a temperature gradient in a semiconductor.

### 3. Degenerate Case

Let us now consider a semiconductor with energy gap  $\Delta E$  but this time make the assumption that both electrons and holes are highly degenerate.<sup>14</sup> For this case then the electrons follow Fermi-Dirac statistics with the distribution function

$$f_0 = [\exp(E - E_f)/kT + 1]^{-1},$$

where  $E$  is the electron energy and  $E_f$  the Fermi energy. The hole distribution function is then  $1 - f_0(E, E_f) = f_0^+(E', E_f')$ , where we have used the energy coordinate transformation  $E = -\Delta E - E'$ ,  $E_f = -\Delta E - E_f'$  such that

$$f_0^+ = [\exp(E' - E_f')/kT + 1]^{-1}.^{15,16}$$

Positive hole energies are measured down from the top of the conduction band ( $E' = 0$ ), and  $E_f'$  is the Fermi energy of the holes. It is now easily seen that the condition for the degeneracy of the electrons, i.e.,  $(E_f/kT) \gg 1$ , and that of the holes,  $(E_f'/kT) \gg 1$  cannot simultaneously be met if the relation  $E_f = -\Delta E - E_f'$  is to be satisfied.<sup>17</sup> It can only be satisfied if  $\Delta E$  is negative, i.e.,  $-\Delta E$ . Physically this simply means that the conduction and valence bands overlap by the amount  $|\Delta E|$ . In the classical case it was easy enough to find expressions for the average energy of the carriers, and their equilibrium concentrations. Matters are no

longer so simple for degenerate carriers, expressions for  $\epsilon$ ,  $n$ , and  $(\partial n/\partial T)$  cannot be obtained in a closed form. The expressions for the average energy, carrier density, etc., must now be obtained in power series expansions of the reduced Fermi energy. In order to reduce the problem to manageable proportions and to obtain a tractable expression for the Fermi energy, we assume equal hole and electron masses. This results in a number of simplifications:  $E_f = E_f' = |\Delta E|/2$ ,  $(\partial n_1/\partial T) = (\partial n_2/\partial T)$ , and more importantly, the average kinetic energy of the holes may be set equal to that of the electrons, even though the carriers are degenerate. With these simplifying assumptions and the condition of overlapping bands, we can write Eq. 16 in the form,

$$W_x \sigma \left( \frac{\partial T}{\partial x} \right)^{-1} = -e^{-2} \left\{ (\sigma_1 + \sigma_2)^2 \epsilon \left( \frac{\partial \epsilon}{\partial T} \right) + \sigma_1 \sigma_2 (2\epsilon - |\Delta E|) \times \left[ \left( \frac{\partial \epsilon}{\partial T} \right) + 2en^{-1} \left( \frac{\partial n}{\partial T} \right) \right] \right\}, \quad (19)$$

where as above we let  $E_1 = \epsilon$ , and  $E_2 = \Delta E + \epsilon$ ; but now with the difference,  $\Delta E = -|\Delta E|$ .

We now proceed with the calculations of the average energies, concentration of carriers  $n$ , etc., in degenerate statistics. The average energy of an electron or hole may be obtained in a power series expansion in powers of  $(kT/E_f)$  from the expression of the internal energy of electrons

$$U = \epsilon = kT [F_3(E_f/kT)/F_3(E_f/kT)] \quad (\text{see Ref. 18}),$$

where the function  $F_k(E_f/kT)$  is defined by the integral

$$F_k(\eta) = \int_0^\infty [\exp(x - \eta) + 1]^{-1} x^k dx.$$

These functions and their power-series expansions are discussed by McDougall and Stoner,<sup>19</sup> and Wilson.<sup>20</sup> Expressions for  $n$  and  $(\partial n/\partial T)$  are

<sup>12</sup> See Ref. 7, p. 88.

<sup>13</sup> P. J. Price, *Phil. Mag.* **46**, 1252 (1955).

<sup>14</sup> The assumption of high degeneracy simplifies calculations.

<sup>15</sup> See Ref. 11, p. 168.

<sup>16</sup> A. H. Wilson, *The Theory of Metals*, (Cambridge University Press, Cambridge, England, 1953), 2nd ed. p. 211, Eq. 8.511.1, and, p. 233.

<sup>17</sup> We are indebted to J. Marburger for raising and clarifying this point.

<sup>18</sup> See Ref. 16, p. 147, Eq. 623.1.

<sup>19</sup> J. McDougall and E. C. Stoner, *Phil. Trans. Roy. Soc. London* **A237**, 67 (1938), Eq. 5.1.

<sup>20</sup> See Ref. 16, p. 332, Eq. A41.6.

obtained from their dependence on  $T$  in intrinsic semiconductors and semimetals:

$$n = 4\pi(2mkT/h^2)^{3/2} F_{3/2}(E_f/kT) \quad (\text{see Ref. 21}).$$

If we make a power-series expansion of the functions  $F_k(\eta)$  for the condition  $E_f/kT \equiv \eta \gg 1$  for  $\epsilon$ ,  $(\partial\epsilon/\partial T)$ ,  $n^{-1}(\partial n/\partial T)$ , etc., we obtain the following expressions,

$$\left. \begin{aligned} \epsilon &= \left(\frac{3}{5}\right)kT(\eta + \pi^2 2^{-1}\eta^{-1} + \dots), \\ \left(\frac{\partial\epsilon}{\partial T}\right) &= \left(\frac{3}{5}\right)\pi^2 k\eta^{-1} + \dots, \\ \epsilon\left(\frac{\partial\epsilon}{\partial T}\right) &= \left(\frac{3}{5}\right)^2 \pi^2 k^2 T \left(1 + \left(\frac{2}{15}\right)\pi^2 \eta^{-2} + \dots\right), \\ n^{-1}\left(\frac{\partial n}{\partial T}\right) &= 4^{-1}\pi^2 T^{-1}\eta^{-2} + \dots, \\ \epsilon n^{-1}\left(\frac{\partial n}{\partial T}\right) &= \left(\frac{3}{5}\right)4^{-1}\pi^2 k\eta^{-1} + \dots, \\ \epsilon^2 n^{-1}\left(\frac{\partial n}{\partial T}\right) &= \left(\frac{3}{5}\right)^2 4^{-1}\pi^2 k^2 T(1 + \pi^2 \eta^{-2} + \dots). \end{aligned} \right\} (20)$$

If we substitute Eq. 20 in Eq. 19, omit all common numerical constants in the expansions of Eq. 20, and drop all terms of order higher than  $\eta^{-1}$ , we get,

$$W_x \sigma \left(\frac{\partial T}{\partial x}\right)^{-1} = -2e^{-2}[(\sigma_1 + \sigma_2)^2 k^2 T + \sigma_1 \sigma_2 (6k^2 T - 3|\Delta E|k\eta^{-1})]. \quad (21)$$

Making the substitution  $|\Delta E| = 2E_f = 2\eta kT$  in Eq. 21 we find that the ambipolar term reduces to zero, leaving us with the individual contribution of the electrons and holes to the heat conductivity,

$$W_x \sigma (\partial T/\partial x)^{-1} = -2e^{-2}k^2 T(\sigma_1 + \sigma_2)^2. \quad (22)$$

This result, obtained on the basis of a very simple model, agrees within the assumptions made, with the exact calculations of Madelung,<sup>22</sup> and Dannhäuser.<sup>23</sup> They show the ambipolar

contribution for a semimetal (negative energy gap) to be extremely small and to be of order  $\eta^{-2}$  and higher.

### III. CONCLUSIONS

The interpretation of the results for the classical case present no difficulties.<sup>24</sup> The temperature gradient in the semiconductor and its concomitant density gradient produce a flow of carriers. If there is to be no net current flow, ( $j_x = 0$ ), an electric field must be set up to oppose the flow of carriers. This field changes the individual flows of the holes and electrons if their mobilities are not equal such that the net current becomes zero (we assume here equal number of electrons and holes). Despite zero net-current flow the net-energy flow does not reduce to zero, because the average energy of the carriers drifting along the temperature-density gradient is greater than that of the carriers drifting back under the influence of the retarding field  $\mathcal{E}_x$ . If we assume for simplicity's sake that both carriers have the same mobility, ( $n_1$  again being equal to  $n_2$ ), the individual currents exactly compensate each other, and the boundary condition of no net current is met without a compensating field  $\mathcal{E}_x$ . In other words the carriers drift under the sole influence of the combined temperature density gradients. Eq. 14 shows quite clearly that  $\mathcal{E}_x$  reduces to zero if  $n_1\mu_1 = n_2\mu_2$ .<sup>25</sup> We can make an estimate of the energy transported under these conditions by making use of the average drift velocity of the carriers, which are easily obtained from Eq. 6 and 7. The drift velocity,  $u_t$ , due to the temperature gradient is equal to  $D^t(\partial T/\partial x)$ , and the drift velocity,  $u_n$ , due to the density gradient is  $D(\partial n/\partial x)$ . The energy to create an electron hole pair, the "ionization energy,"<sup>26</sup> is  $E_1 + E_2 = |\Delta E| + \epsilon_1 + \epsilon_2$ . Therefore, the rate at which energy drifts down the temperature-density gradient with a pair is  $(E_1 + E_2)(u_t + u_n)$ . It is now easily verified with Eqs. 6 and 7, and the expression<sup>26</sup> for  $(\partial n/\partial T)$ , that the above expression for the rate of energy transport is indeed the ambipolar contribution to the thermal conductivity.<sup>27</sup> Thus the origin of the

<sup>24</sup> See Ref. 23, p. 527.

<sup>25</sup> Note that according to our definition  $(\mu_1/|\mu_1|) = -(\mu_2/|\mu_2|)$ .

<sup>26</sup> See Sec. 2.

<sup>27</sup> Compare with Refs. 13 and 28, p. 9.

<sup>21</sup> See Ref. 11, p. 79.

<sup>22</sup> See Ref. 7, p. 88.

<sup>23</sup> F. Dannhäuser, Z. Physik 166, 519 (1962), Eq. 14.

various terms in the expression for the ambipolar term in Eq. 18 are easily accounted for. At first thought, one would expect this contribution to be linear in  $\Delta E$ , but the term proportional to  $(\Delta E)^2$  can now be traced directly to that part of the energy transport caused by the density gradient.

The general arguments given in the preceding paragraph concerning the drift of electron-hole pairs under the influence of temperature and density gradients is unaffected by the degree of degeneracy of the carriers. Equation 16, which describes the energy transport by electrons and holes, is equally applicable to both classical and degenerate carriers. However, in order to see why the ambipolar contribution to the heat conductivity for the latter is nonexistent (to a first approximation), we have to draw on some results of solid-state theory. These results are actually implicit in the assumptions made in Sec. 3. We assumed overlapping bands, and the Fermi level midway between the top of the valence and the bottom of the conduction band. Consequently all energy levels in both bands are filled with electrons up to the Fermi level at  $T=0^\circ\text{K}$ . But the unoccupied states in the valence band between the top of the band and the Fermi level (i.e., in the corners of the first Brillouin zone of a simple cubic lattice, say)

behave like holes.<sup>28</sup> At elevated temperatures electrons in the conduction band and holes in the valence band are excited into higher states. We can now easily visualize a "free" electron and a "free" hole which exist literally side by side, i.e., occupy the same energy level, but in different bands. Whereas in the classical case electrons and holes were of necessity separated by at least the "ionization energy,"  $\Delta E$ , we find that the above mentioned pair transports no ionization energy. We can further imagine all free electrons and holes in their respective bands paired off in the fashion described. Thus on the average there is no ambipolar contribution to the heat conductivity. We also note that if we take the average total energy of an electron hole pair,  $E_1 + E_2 = \Delta E + \epsilon_1 + \epsilon_2$ , let  $\epsilon_1 = \epsilon_2 \approx |\Delta E|/2$ , and put  $\Delta E = -|\Delta E|$ ,  $E_1 + E_2$  reduces to zero. This physical picture of the ambipolar effect in semimetals does seem to be a fairly accurate one, since the exact results<sup>29</sup> show the effect to be smaller by a factor of  $\eta^{-2} \approx (1/100)$  than the straightforward electron and hole conduction.

<sup>28</sup> J. M. Ziman, "Electrons in Metals" in *A Short Guide to the Fermi Surface* (Taylor and Francis Ltd., London, 1962), p. 37.

<sup>29</sup> See Ref. 23.